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Desorption study of spent activated carbon filter to investigate micropollutants in tap water

수도수에 잔류하는 미량오염물질 규명을 위한
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Abstract

Desorption of micropollutants such as pharmaceuticals and personal care products (PPCPs) and endocrine disrupting compounds (EDCs) from a spent activated carbon using ultrasonic irradiation and organic solvent extraction were investigated. First, to optimized the desorption condition, this study compared several extraction solvents, appropriate amount of solvent, and sonication time. The optimized condition for desorption of micropollutants was found to be 800 mL of acetonitrile solvent, and 90 min of sonication for 1 g of PAC at 30^{o}C. Then, to examine which micropollutants were adsorbed in the powdered activated carbon (PAC) filter used in the commercial water purifier, this optimized desorption condition was applied to extract the micropollutants from spent PAC filter. Total 11 micropollutants (caffeine, acetaminophen, sulfamethazine, sulfamethoxazole, metoprolol, carbamazepine, naproxen, bisphenol-A, ibuprofen, diclofenac, and triclocarban) were analysed from spent carbon filter. Among the micropollutants, caffeine, metoprolol, naproxen, and diclofenac had higher detection frequencies (>60%), and sulfamethazine, metoprolol and ibuprofen were only detected in the carbon filters, but not in the tap water, indicating that these micropollutants might exist less

than detection level in the tap water, but accumulated in the carbon filter. Also, the regional patterns where the water purifiers are used were examined by identifying micropollutant detection patterns from spent carbon filter with various regions in Korea. The result showed that higher concentration of micropollutants were detected from the carbon filter collected from the Han river and Nakdong river basins with large population. Also, the level of micropollutants were higher where advanced oxidation process (AOP) are adopted in the drinking water treatment plants (WTPs), indicating that AOP process is effective for the removal of micropollutants. When compared according to different pore size filters, the desorption amount was higher from the filter which pore size is 10 times smaller than the other, indicating that higher amount of micropollutants can be adsorbed in smaller pore size filter.

Keywords: Micropollutants; Activated carbon filter; Desorption; Optimization; Tap water

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I. Introduction

1.1. Micropollutants in the environment

Surface water is commonly used as a drinking water source in areas with growing urban populations (Stackelberg et al., 2007). The 20 % of population were concentrated in Seoul, capital of Korea. Micropollutants such as pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting compounds (EDCs) have been found in wastewater effluents, surface water and even tap water at ng/L to μg/L (Halling-Sorensen et al., 1998; Vanderford et al., 2003; Kim et al., 2007; Kasprzyk-Hordern et al., 2008; Benotti et al., 2009; Rahman et al., 2009). Micropollutants can flow into water environment from various sources, such as pharmaceutical factories, household, hospital effluent, antibiotics to livestocks, agricultural effluents, aquaculture and landfill leachate (Focazio et al., 2008) (Figure 1). Excessive amount of pharmaceuticals are produced and expired pharmaceuticals are thrown out. People can get some over-the-counter medications (e.g. acetaminophen, ibuprofen, and naproxen) easily in pharmacy which are available without prescriptions.

Also, large amount of them were exposed to environment by unappropriate disposal. They cannot be removed fully in conventional water treatment and residual can be released to the aquatic environment (Ratola et al., 2012). Even at very low levels in surface water or drinking water, micropollutants can have adverse health impact to ecosystem due to chronic exposure (Westerhoff et al., 2005; Nam et al., 2014a).

Previous studies reported that some micropollutants such as acetaminophen, caffeine, naproxen and ibuprofen can be effectively removed (more than 80%) in water treatment plants (Yu et al., 2006; Gomez et al., 2007; Nam et al., 2014b). However, some micropollutants such as carbamazepine, diclofenac, clofibric acid, and metoprolol have showed poor removal efficiency (Yu et al., 2006; Gomez et al., 2007; Benotti et al., 2009; Nam et al., 2014b), indicating that these compounds are not removed completely in water treatment plants and flow into water stream.

In this study, the 11 micropollutants were selected based on their domestic usages, occurrences in surface water, and in tap water in Korea (Table 1). The selected micropollutants are produced significantly annually, especially caffeine, bisphenol-A and the over-the counter drugs. Therefore, they can be detected frequently in surface water in Korea, and

some of them are detected even in tap water or have possibility to be detected in tap water (Table 1).

Table 1. Annual domestic productions, occurrences of study micropollutants in surface waters and tap water in Korea

Compounds	Annual production (ton/yr)	Occurrences (ng/L)	
		Surface water	tap water
Diclofenac (DCF)	5.9[a]	21-383[d]	ND[d]
Ibuprofen (IBU)	149.3[b]	11-38[f]	ND[d]
Naproxen (NPX)	43.1[b]	20-483[f]	ND[d]
Carbamazepine (CBM)	8.9[a]	3-344[d]	1-48[e]
Metoprolol (MTP)	0.8[b]	2.3-164.5[g]	ND[d]
Sulfamethoxazole (SMZ)	61.3[a]	8-54[d]	ND[d] / 2-4[e]
Sulfamethazine (SMA)	13.7[a]	4-309[d]	ND[d] / 2-3[e]
Acetaminophen (ACT)	754.9[a]	2-965[d]	17-55[e]
Caffeine (CFF)	1823.6[b]	6-1475[d]	3-249[d]
Triclocarban (TCB)	-[h]	-	-
Bisphenol-A (BPA)	1,480[c]	0.08-1.52[d]	80-100

a: National Institute of Environmental Research, 2007; b: Korean Pharmaceutical Manufacturers Association, 2003; c: KME, 2007; d: National Institute of Environmental Research, 2011; e: National Institute of Environmental Research, 2014; f: Kim et al., 2007; g: Nam et al., 2014; h: unknown data

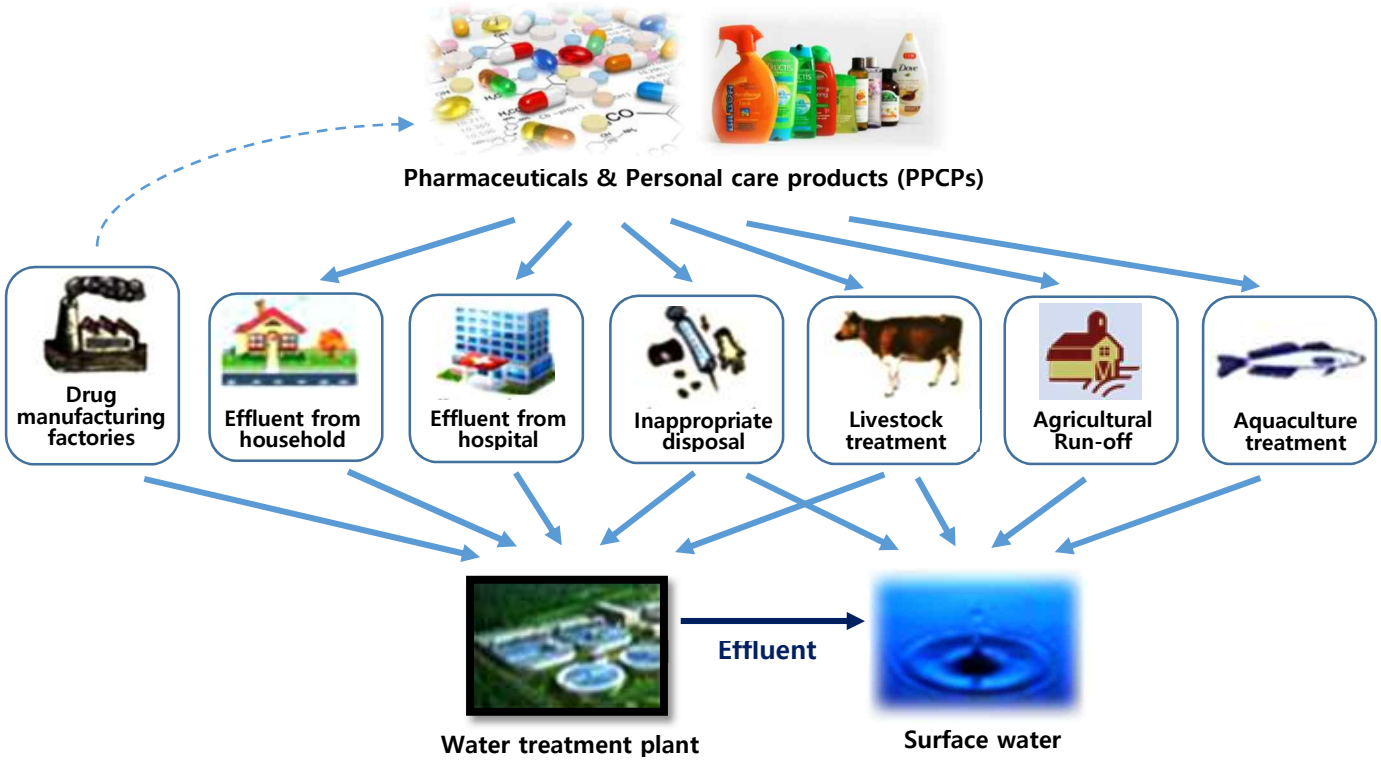

Figure 1. Release pathway of micropollutants into surface water

1.2. Activated carbon adsorption and desorption

Activated carbon such as granular activated carbon (GAC) or powder activated carbon (PAC) can remove micropollutants (e.g. taste and odor compounds, pesticides and pharmaceuticals) effectively by adsorption process (Ternes et al., 2002; Westerhoff et al., 2005). Adsorption is a process which utilizes physical, chemical and electrostatic interactions between the contaminants and adsorbent (Karanfil et al. 2004). It is being widely used in water treatment plants because it is cost-effective, simple, and has high efficiency of removal (Sotelo et al., 2012). However, adsorption efficiencies vary by physicochemical property such as hydrophobicity of compounds, pore size and amount of adsorbent, contact time, pH, and competition with natural organic matter (Yoon et al., 2003; Snyder et al., 2007; Nam et al., 2014a).

There are various techniques to regenerate GAC, such as thermal regeneration (Ania et al., 2004; Ledesma et al., 2014), solvent regeneration (Zhou et al., 2015), microwaved-induced regeneration (Ania et al., 2004; Ania et al., 2005a) and catalytic wet oxidation (Gonzalez et al., 2002). However, these techniques have the limitations

such as low regeneration efficiencies, high energy consumption, high cost, generation of toxic products and potential secondary pollution (Zhou et al., 2015). Also, thermal regeneration which is widely used regeneration technology can cause degradation of pore structure, and significant amount of carbon loss (Ania et al., 2005b; Li et al., 2015). Therefore, the effective regeneration technique is needed. Chemical regeneration can be conducted rapidly with no carbon consumption (Lu et al., 2011). The solubility of compounds to solvent and affinity to adsorbent surface influence on regeneration efficiency (Karanfil and Dastgheib, 2004) . However, there have been no attempt to desorb micropollutants from spent activated carbon filter used in commercial water purifier.

In Korea, there is high percentage of water purifier usage due to the widespread hesitation of using tap water as drinking water directly (Yoo, 2005). The reason for not drinking tap water is mostly indefinite anxiety, such as distrust of water tank and water pipe. Most people drink purified water instead of tap water in Korea. Most water purifiers adopt activated carbon filter as pre- or post-treatment process. The micropollutants such as PPCPs, EDCs, and taste and odor compounds existed in the tap water as trace levels can be accumulated in activated carbon filter. Therefore,

the adsorbed micropollutants can be identified by the desorption process from spent activated cabon filters.

1.3. Objectives

The objectives of this study were: (1) to examine the optimized desorption method to desorb micropollutants in spent carbon filter; (2) to examine which micropollutants are exist in field carbon filters, and investigate the tap water quality in each reason indirectly; and (3) to investigate the regional pattern where the water purifiers are used was examined by identifying the contaminants detection patterns from spent activated carbon filter.

II. Materials and Methods

2.1. Chemicals and materials

Acetaminophen (ACT), caffeine (CFF), carbamazepine (CBM), diclofenac (DCF), ibuprofen (IBU), naproxen (NPX), metoprolol (MTP), sulfamethoxazole (SMZ), sulfamethazine (SMA), bisphenol-A (BPA), triclocarbon (TCB) were purchased from Sigma-Aldrich (Korea), of which the physical and chemical properties are shown in Table 2. All chemicals 100 mg were dissolved in 100 mL methanol to make the stock solutions, and were kept in 4^{o}C refrigerator to prevent biodegradation. $^{13}C_6$-sulfamethoxazole and $^{13}C_6$-naproxen (Cambridge Isotope Laboratories, Cambridge, UK) were used as internal standards to compensate for matrix effects. Methanol (LC-MS grade), and acetonitrile were obtained from Fisher Scientific (USA). Coconut shell-based powdered activated carbon (PAC, Coway Co. Korea, 80-325 mesh) was used as an adsorbent, and prepared as a solution of 1 g/L hydrated for 24 h in distilled water to activate the surface of PAC.

Table 2. Physico-chemical properties of target micropollutants

Compounds	Molar formula	$LogK_{ow}$	pK_a	General use
Diclofenac (DCF)	$C_{14}H_{11}Cl_2NO_2$	3.91[a]	4.15	Anti-inflammatory
Ibuprofen (IBU)	$C_{13}H_{18}O_2$	3.64[a]	4.51	Anti-inflammatory
Naproxen (NPX)	$C_{14}H_{14}O_3$	2.84[a]	4.2	Anti-inflammatory
Carbamazepine (CBM)	$C_{15}H_{12}N_2O$	2.47[b]	7	Anticonvulsant
Metoprolol (MTP)	$C_{15}H_{25}NO_3$	1.88[b]	9.68	β-blocker
Sulfamethoxazole (SMZ)	$C_{10}H_{11}N_3O_3S$	0.68[a]	5.7	Antibiotic
Sulfamethazine (SMA)	$C_{12}H_{14}N_4O_2S$	0.62[c]	2.6/7.7	Antibiotic
Acetaminophen (ACT)	$C_8H_9NO_2$	0.46[d]	9.38	Antipyretic
Caffeine (CFF)	$C_8H_{10}N_4O_2$	-0.5[a]	14	Stimulant
Triclocarban (TCB)	$C_{13}H_9Cl_3N_2O$	4.2-6[e]	12.7	Anti-microbial disinfectant
Bisphenol-A (BPA)	$C_{15}H_{16}O_2$	3.4[f]	9.59	Plasticizer

a: Bones et al., 2006; b: Gros et al., 2006; c: Henry et al., 1976; d: Stackelberg et al., 2007; Sabourin et al., 2009; e: Snyder and Allene, 2009; f: Staples et al., 1998

2.2. Experimental procedures

2.2.1. PAC saturation with micropollutants

A series of 2 L beakers containing hydrated 1 g/L PAC with distilled water were installed in a jar tester. The initial concentration 10 mg/L of each 11 micropollutants was added to beakers. A rapid mixing (140 rpm) ensured a vigorous mixing solution state and accelerated the adsorption process. The micropollutants were saturated in PAC by agitating for 90 min. The exhausted PAC was separated by filtration using 0.45-μm GF/C filter (Whatman, UK), and dried in room temperature for 24 h. The result showed that these micropollutants were fully adsorbed in PAC filter about 90 to 100 % (Table 3).

Table 3. The result of the PAC saturation process (1 g/L PAC, 10 mg/L of compounds, mixing time 90 min, mixing speed 140 rpm, temperature 20℃)

Compounds	C_0 (mg/L)	C_t (μg/L)	Adsorption (%)
Caffeine		62.24	99.38
Acetaminophen		38.89	99.61
Sulfamethazine		598.08	94.02
Sulfamethoxazole		353.28	96.47
Metoprolol		263.48	97.37
Carbamazepine	10	139.92	98.60
Naproxen		27.24	99.73
Bisphenol-A		1.43	99.99
Ibuprofen		184.41	98.16
Diclofenac		104.24	98.96
Triclocarban		50.16	99.50

2.2.2. Desorption test for optimization

Table 4 shows the experiment conditions in each parameter for optimization of desorption. 4 parameters were examined in this study, mixing tools such as stirrer, shaker or sonicator, mixing time, extraction solvent, and solvent amount. Batch desorption experiments were carried out in the stirrer, shaker or sonicator. A rapid mixing 300 rpm were

provided by a shaker, and 400W sonication power (frequency 40 kHz) ensured a strong stimulation for desorption. Methanol and acetonitrile was used as extraction solvent. 10 mM $CaCl_2$ and pH adjusted deionized water were also compared with extraction solvent. Different volumes of organic solvent (200, 400, and 800 mL) was used to desorb the micropollutants from exhausted PAC. To find efficient desorption time, different sonication time (60, 90, and 120 min) were also compared (Table 4).

After desorption process, the 10 mL sample was withdrawn and filtered through 0.45-μm membrane filter. Also, the sample was concentrated for 24 hours using centrifugal concentrator (CVE-3100, EVELA, Japan), and then was eluted by 1.0 mL methanol.

Table 4. Environmental conditions of desorption experiments for optimization

Condition		adsorbed conc. (ppm)	adsorbent (g/L)	Solvent	Contact time	Temperature (°C)
Tool	Stirrer (120 rpm)	~10	1	200 mL methanol	90 min	20
	Shaker (300 rpm)	~10	1	200 mL methanol	90 min	20
	Sonicator (400 W)	~10	1	200 mL methanol	90 min	20
Time	30 min	~10	1	200 mL methanol	30 min (shaker)	20
	60 min	~10	1	200 mL methanol	60 min (shaker)	20
	90 min	~10	1	200 mL methanol	90 min (shaker)	20
Solvent	pH 12 DW	~10	1	400 mL distilled water	60 min	30
	10mM $CaCl_2$	~10	1	400 mL 10mM CaCl2	60 min	30
	Methanol	~10	1	400 mL methanol	60 min	30
	Acetonitrile	~10	1	400 mL acetonitrile	60 min	30
Solvent amount	200 mL	~10	1	200 mL acetonitrile	60 min	30
	400 mL	~10	1	400 mL acetonitrile	60 min	30
	800 mL	~10	1	800 mL acetonitrile	60 min	30

2.2.3. Collecting field water filters

In Korea, there are 4 major river streams, (the Han River, Geum River, Yeongsan River and Nakdong River) (Figure 2). Especially, metropolitan cities such as Seoul, Busan and Daegu cities are located in the Han river and Nakdong river basins. The population in Seoul near Han river basin is approximately 10 million in an area of 605.18 km^2 (a population density of 16,659 capita km^{-2}) and Nakdong river basin includes 2 condensed cities [‘Daegu’ city with a population of 2,518,467 in an area of 883.63 km^2 (2,857 capita km^{-2}), ‘Busan’ city with a population more than 3 million in an area of 769.82 km^2 (4628 capita km^{-2})] and many industrial complexes. The population ranking of Seoul, Busan and Daegu took first, second and fourth place respectively in Korea.

Usually, the spent filters were replaced with a new one after every 4 to 6 months. The filter samples were collected from the homes around the 4 major river basins. The filters were collected from the houses around the water treatment plants. 4 activated carbon filters were collected from houses which is connected to each water treatment plants.

Total 100 spent field filters (40 filters from Han River basin, 12 filters from Geum River basin, 16 filters from Yeongsan River basin, 32 filters

from Nakdong River basin) were collected from the houses located in each river basin (Figure 2). The collected filters were then grouped according to the existence of advance oxidation process facility in their water treatment plants (Table 5). 7 WTPs have advanced oxidation process among 10 WTPs in Han river basin. 5 WTPs have advanced oxidation process among 8 WTPs in Nakdong river basin (Table 5). There were no advanced oxidation process in WTPs in Geum river or Youngsan river basins. 2 kinds of water filters were collected in each WTPs areas, they were different in filter length and pore size (Table 6). The 50 filters have pore size around 10 μm and the length is 16 cm, other 50 filters have pore size around 1 μm and the length is 8 cm (Table 6).

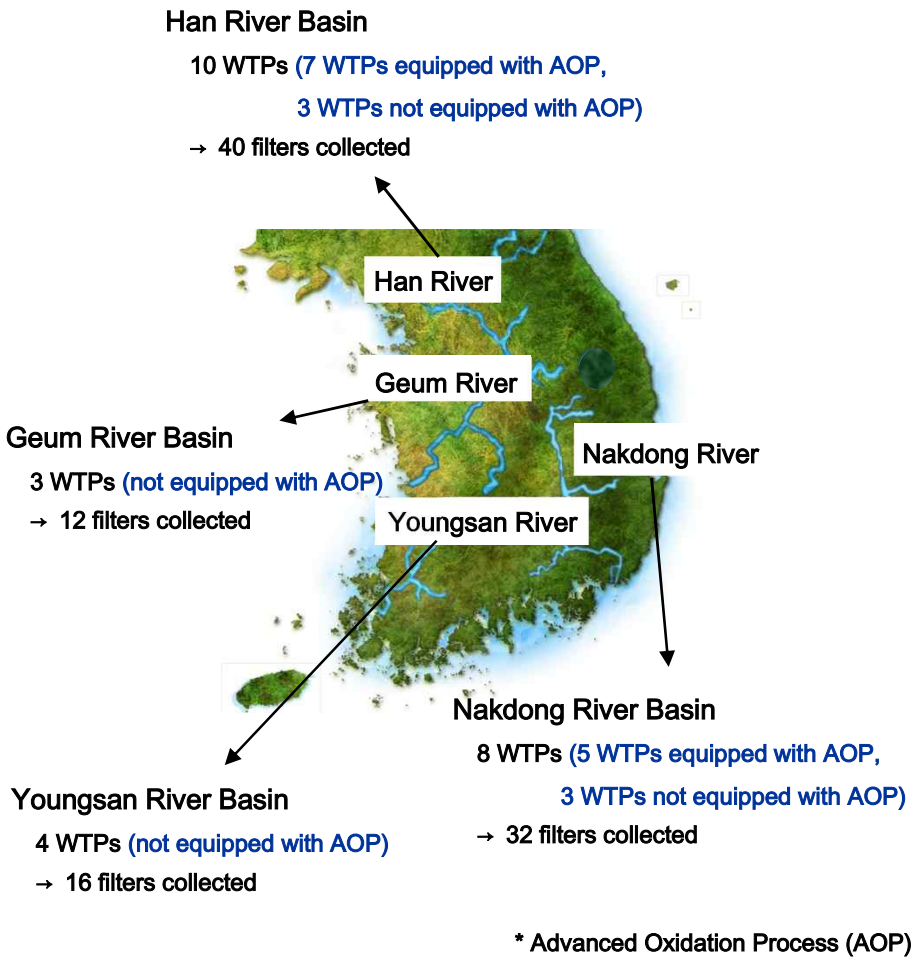

Figure 2. Sampling area of field filters.

Table 5. Treatment process of water treatment plants in sampling area 4 river streams

Water stream	area		WTPs	Quantity (m^3/year)	Treatment process	AOP process
Han river	Seoul	Seoul	WTP1	425,895,702	flocculation+sedimentation+filtration	Ozone + BAC
			WTP2	166,414,280	flocculation+sedimentation+filtration	Ozone + BAC
			WTP3	67,507,098	flocculation+sedimentation+filtration	Ozone + BAC
			WTP4	147,705,514	flocculation+sedimentation+filtration	Ozone + BAC
			WTP5	295,764,897	flocculation+sedimentation+filtration	Ozone + BAC
	Gyeonggi-do	Seongnam-si	WTP6	85,761,814	flocculation+sedimentation+filtration	- [a]
		Gimpo-si	WTP7	38,089,764	flocculation+sedimentation+filtration	Ozone + BAC
	Gangwon-do	Chuncheon-si	WTP8	25,437,350	flocculation+sedimentation+filtration	-
		Wonju-si	WTP9	22,294,882	flocculation+sedimentation+filtration	Ozone + BAC
		Gangneung-si	WTP10	13,259,200	flocculation+sedimentation+filtration	-
Geum river	Chungchengbuk-do	Cheongju-si	WTP11	30,964,427	flocculation+sedimentation+filtration	-
	Daejeon		WTP12	120,705,390	flocculation+sedimentation+filtration	-
	Jeollabuk-do	Iksan-si	WTP13	27,590,970	flocculation+sedimentation+filtration	-
Youngsan river	Gwangju		WTP14	70,629,770	flocculation+sedimentation+filtration	-
			WTP15	84,371,731	flocculation+sedimentation+filtration	-

	Jeollanam-do	Yeosu-si	WTP16	27,398,629	flocculation+sedimentation+filtration	- [a]
		Suncheon-si	WTP17	14,282,714	flocculation+sedimentation+filtration	-
Nakdong river	Gyeongsangbuk-do	Gyeongsan-si	WTP18	21,648,066	flocculation+sedimentation+filtration	-
	Gyeongsangnam-do	Changwon-si	WTP19	84,986,000	flocculation+sedimentation+filtration	Ozone + BAC
		Jinju-si	WTP20	16,024,396	flocculation+sedimentation+filtration	-
		Gimhae-si	WTP21	34,933,097	flocculation+sedimentation+filtration	Ozone + BAC
	Busan		WTP22	40,815,040	flocculation+sedimentation+filtration	Ozone + BAC
			WTP23	146,633,500	flocculation+sedimentation+filtration	Ozone + BAC
			WTP24	1,392,566	Sedimentation+sand filtration	-
			WTP25	197,392,000	flocculation+sedimentation+filtration	Ozone + BAC

[a]-: Advanced oxidation process is not available

Table 6. Characteristics of 2 kinds of activated carbon filters used in water purifiers

	Filter A	Filter B
Pore size	~10 μm	~1 μm
Length	16 cm	8 cm
Carbon amount	130 g d.w.	60 g d.w.

2.2.4. Desorption of field filters

Total 100 spent field carbon filters obtained from different regions in Korea were cutted into slices of which the thickness are less than 3 mm. Then, the cutted filters were dried for 24 hours to remove water from the filters. After drying, they were ground by blender and fine particle powder was obtained. The ground field filters were used for the desorption experiment as shown in Fig. 3. 400 mL of acetonitrile for small size filters and 800 mL of acetonitrile for larger size filters were used as extraction solvent. Then, they were sonicated for 90 min with 400 W sonication intensity. The 50 mL of sample was withdrawn and filtered through 0.45-μm filter. Samples were concentrated for 24 hours using centrifugal concentrator (CVE-3100, EVELA, Japan) and eluted by methanol 1 mL.

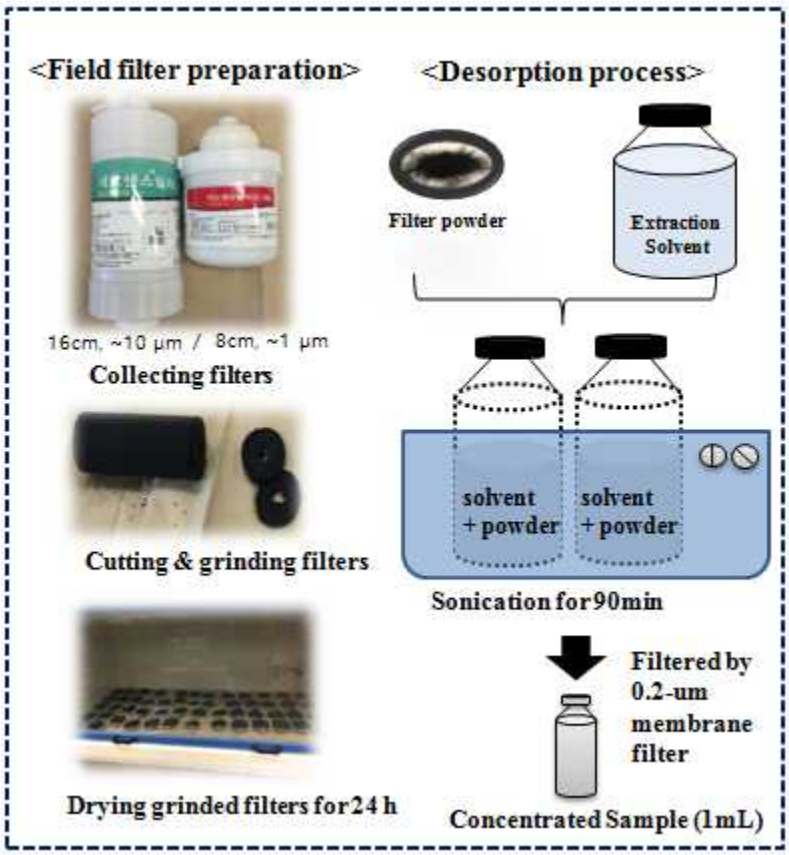

Figure 3. Schematic diagram of desorption experiment

2.3. Analytical Methods

The target micropollutants were analyzed by UPLC (Nexera, Shimadzu, Kyoto, Japan) connected to a triple quadrupole mass spectrometer (API-4000, Forster City, Canada) with an electron ion spray source working in both positive and negative modes. The target micropollutants were separated with a reverse phase C_{18} column (Luna 3μm; 150 x 20 mm, Phenomenex, Torrance, Canada). The flow rate was 0.2 mL/min, and the injection volume was 10 μL. The isocratic mobile phase was 95:5 methanol:water with 10 mM ammonium formate and 0.3% formic acid (v/v) in the positive mode, and 98:2 methanol:water with 5 mM ammonium acetate (v/v) in the negative mode (Nam et al. 2014). By ionization, the target compounds were separated into negative (ACT, BPA, DCF, IBU, NPX and TCB) or positive (CBM, CFF, MTP, SMA, and SMZ) ion groups. The optimized ion pairs of the 11 micropollutants and MS collision conditions are shown in Table 7.

For quality assurance/quality control (QA/QC), the recoveries of the extracted samples were calculated by comparing the spiked water samples with standard samples. It is obtained the limit of detection (LOD) and limit of quantification (LOQ) calculated using a signal to noise (S/N)

ratios of 3 and 10. LOD and LOQ of the samples were in the range of 0.07-0.51 ng/L and 0.25-1.69 ng/L. Method detection limit (MDL) was estimated with 7 replicates using 1 and 2 ng/L of standard analytes samples. The MDLs were in the range 0.4-2.65 ng/L and the recoveries of internal standards were in the range 96-119% throughout the experiments (Table 8).

Table 7. LC-MS/MS conditions for the analysis of target compounds

Compounds	Precursor ion (m/z)	Product ion (m/z)	Declustering potential (mV)	Collision energy (mV)	Collision cell exit potential (mV)
Positive mode					
SMZ	254.011	156	61	21	16
		92.1	61	37	10
CBM	237.134	194.1	61	25	18
		191.8	61	31	20
CFF	194.99	137.9	56	25	14
		137.7	56	25	12
MTP	268.087	116.1	81	25	12
		121.1	81	31	12
SMA	279.001	186	61	23	16
		161.8	61	23	16
^{13}C-SMZ[a]	259.987	98.1	61	35	10
		114	61	31	12
Negative mode					
IBU	205.227	158.8	–45	–10	–9
		160.8	–45	–10	–9
ACT	149.942	106.9	–65	–24	–5
		108	–65	–20	–5
BPA	226.923	211.9	–70	–26	–15
		211	–70	–26	–11
DCF	293.794	249.9	–45	–14	–17
		214	–45	–28	–15
NPX	228.928	185	–30	–10	–11
		168.9	–30	–36	–11
TCB	313.147	159.7	–100	–18	–11
		169.7	–30	–22	–9
^{13}C-NPX[b]	233.17	169.8	–30	–22	–11
		168.8	–30	–36	–11

a:^{13}C-sulfamethoxazole (internal standard)
b:^{13}C-naproxen (internal standard)

Table 8. MDLs of analytes and recoveries in water samples

Compounds	MDL (ng/L)	RSD[b] (%)	Recovery (%)[a]		
			Mean ± SD	max	min
Caffeine	0.23	3.11	114.38 ± 5.01	118.75	105.15
Acetaminophen	0.53	6.61	109.83 ± 5.08	117.15	102.22
Sulfamethazine	0.15	2.31	103.10 ± 2.39	106.47	98.98
Sulfamethoxazole	0.08	1.07	115.49 ± 1.24	116.94	113.27
Metoprolol	0.28	3.46	110.01 ± 6.25	119.05	101.98
Carbamazepine	0.26	3.50	114.93 ± 3.00	118.17	110.51
Naproxen	0.14	2.08	109.24 ± 2.27	111.80	106.26
Bisphenol-A	0.27	2.75	104.18 ± 2.87	108.40	100.24
Ibuprofen	0.21	3.27	102.86 ± 3.37	107.99	98.34
Diclofenac	0.42	5.19	106.76 ± 4.95	102.80	116.23
Triclocarban	0.24	2.56	99.39 ± 2.25	103.36	96.31

[a] Recoveries were calculated with the spiked internal standard (10 ng/L); ^{13}C -sulfamethoxazole and ^{13}C-naproxen.
[b] The relative standard deviation (RSD, %) expresses the percentage of standard deviation divided by mean

III. Results and Discussion

3.1. Optimization of desorption

First, the effect of mixing tool for desorption of PPCPs is illustrated in Table 9. Shaker and sonicator were compared for desorption of PPCPs. Sonicator achieved better desorption efficiency than shaker (Table 9). The enhancement effect of sonicator might be mainly due to the cavitation effect between PAC particles produced by ultrasonic irradiation (Zhou et al., 2015). Cavitaion can generate rapid whirlpool by high pressure oscillation, resulting weakening the binding energy between adsorbate and PAC particles (Zhou et al., 2015).

Then, different extraction solvents with pH adjusted distilled water, methanol, and acetonitrile were compared. By adjusting pH 12 of distilled water, micropollutants were hardly desorbed less than 1% (Table 9). This result implies that chemical affinity of solvent and adsorbate is much lower than that of adsorbent and adsorbate. The desorption rate using acetonitrile solvent was significantly higher than using methanol (Table 9). This result might be due to that higher polarity of acetonitrile

encouraged higher adsorption affinity toward polar adsorbate (Martinez and Iverson, 2012).

As also shown in Table 9, the desorption rate was considerably increased with the increasing volume of acetonitrile solvent from 200 to 800 mL, indicating that the desorption can be enhanced by increasing the volume of organic solvent. According to increasing ultrasonic irradiation time from 30 min to 120 min, the desorption amount also increased (Table 9). By considering slight difference between 90 and 120 min, the final optimal condition for desorption was determined as 800 mL of acetonitrile, 90 min of sonication time using sonicator at 30℃ for desorbing 1 g of PAC containing micropollutants. This optimized desorption conditions is a practical, feasible and economically sound method than thermal or bio-regeneration on those compounds due to that the solubility of target compounds to high polarity organic solvent is high and combination with ultrasonic power can stimulate and exceed the power of adsorbate-carbon surface attraction (Zhou et al., 2015).

Table 9. Desorption rate (%) comparison according to each condition for optimization

Desorption (%)		CFF	ACT	SMA	SMZ	MTP	CBM	NPX	BPA	IBU	DCF	TCB
Tool	Stirrer	2.29	0.16	2.59	5.29	0.73	5.52	0.04	0.02	0.67	0.04	0.03
	Shaker	5.34	0.20	2.82	7.39	1.07	6.44	0.12	0.05	1.41	0.10	0.05
	Sonicator	6.52	4.01	7.38	16.66	1.73	8.95	2.44	9.94	12.71	0.37	0.05
Time	30 min	2.80	0.06	0.93	5.45	0.28	2.83	0.03	0.03	0.68	0.01	0.01
	60 min	4.97	0.18	1.93	7.68	0.79	5.51	0.07	0.04	1.20	0.04	0.01
	90 min	7.69	0.30	4.23	11.06	1.61	9.65	0.17	0.07	2.11	0.14	0.07
Solvent	pH 12 DW	0.03	0.01	0.84	5.34	0.00	0.00	0.03	0.53	0.20	0.02	0.02
	10mM $CaCl_2$	0.13	0.00	0.04	0.07	0.13	0.01	0.00	0.01	0.07	0.14	0.10
	Methanol	0.75	1.03	4.91	14.09	4.00	4.64	1.00	10.60	3.30	1.02	0.06
	Acetonitrile	11.55	11.30	15.40	23.49	4.94	17.42	5.81	12.66	22.51	1.21	0.07
Solvent amount	200 mL	6.52	4.01	7.38	16.66	1.73	8.95	2.44	9.94	12.71	0.37	0.05
	400 mL	11.55	11.3	15.4	23.49	4.94	17.42	5.81	12.66	22.51	1.21	0.07
	800 mL	20.68	19.44	22.52	32.1	9.43	23.67	11.36	17.16	32.12	2.64	0.17

3.2. Detection of micropollutants from field water filters by the optimized desorption conditions

Using the optimized desorption conditions, the desorption of micropollutants from field water filters was conducted. Field water filter mean spent activated carbon filter in water purifier which people really used in their houses. The result showed that naproxen, diclofenac, and caffeine were detected more than 80% in 100 field filters and sulfamethazine, sulfamethoxazole, and triclocarban were detected less than 10% (Table 10). Naproxen was the most frequently detected with the highest level of desorption amount from the water filters (Table 10). Kim et al. (2007) showed that naproxen and caffeine are frequently observed micropollutants in both surface water and wastewater treatment plant effluents. Also, caffeine was detected as concentration of 2.5-225 ng/L in untreated and treated drinking water treatment system in U.S. (Wang et al., 2011). Kim et al. (2007) also reported sulfamethoxazole and carbamazepine were detected with significant concentration in surface water in Korea.

The previous study showed that sulfamethoxazole was removed

efficiently by chlorination treatment in conventional drinking water treatment plant, but carbamazepine and caffeine was not removed effectively in chlorination treatment process (Wang et al., 2011). This result indicates that carbamazepine and caffeine can exist in tap water with low level. This is consistent with the result of this study, showing that sulfamethoxazole was not detected and carbamazepine was detected in low level by desorption of filters (Table 10). Benotti et al. (2009) also reported that carbamazepine, sulfamethoxazole are present in tap water in U.S. at 6.8 ng/L, 0.32 ng/L, respectively. In China, 1.3~6.7 ng/L of carbamazepine and 8.0~21.3 ng/L of sulfamethoxazole were reported to be existed in tap water (Leung et al., 2013). In U.S. drinking water treatment system, ibuprofen concentration was almost the same in untreated and treated water sample with a highest concentration of 77.2 ng/L, indicating that these compounds were hardly removed in drinking water treatment system (Wang et al., 2011). Therefore, there is possibility of ibuprofen existing in tap water. The result of this study showed that ibuprofen, metoprolol and declofenac were hardly detected in tap water because they exist in tap water in very low level with less than detection limit (Table 11). However, after they accumulated in filters in water purifier, they were detected from spent activated carbon filters (Table 10).

Therefore, investigating which compounds are exist in tap water by spent carbon filter desorption can be useful method to detect micropollutants in tap water.

Table 10. Detection frequencies and concentration of micropollutants from spent activated carbon filters

	CFF	ACT	SMA	SMZ	MTP	CBM	NPX	BPA	IBU	DCF	TCB
Freq.[a](%)	88.00	14.00	2.00	-	67.00	20.00	100.00	47.00	47.00	97.00	6.00
Mean ± SD (ng/g carbon)	0.11 ±0.12	0.06 ±0.03	0.15 ±0.08	-	0.25 ±0.25	0.13 ±0.14	0.92 ±1.40	0.68 ±1.31	0.30 ±0.45	0.51 ±0.81	0.41 ±0.61
Median (ng/g carbon)	0.07	0.06	0.15		0.15	0.05	0.40	0.33	0.07	0.22	0.22
Min. (ng/g carbon)	0.01	0.03	0.09	0.00	0.02	0.02	0.02	0.03	0.02	0.03	0.04
Max. (ng/g carbon)	0.63	0.10	0.20	0.00	1.05	0.59	8.76	8.76	1.91	5.15	1.63

[a]Freq. : detection frequency (%)
N=100

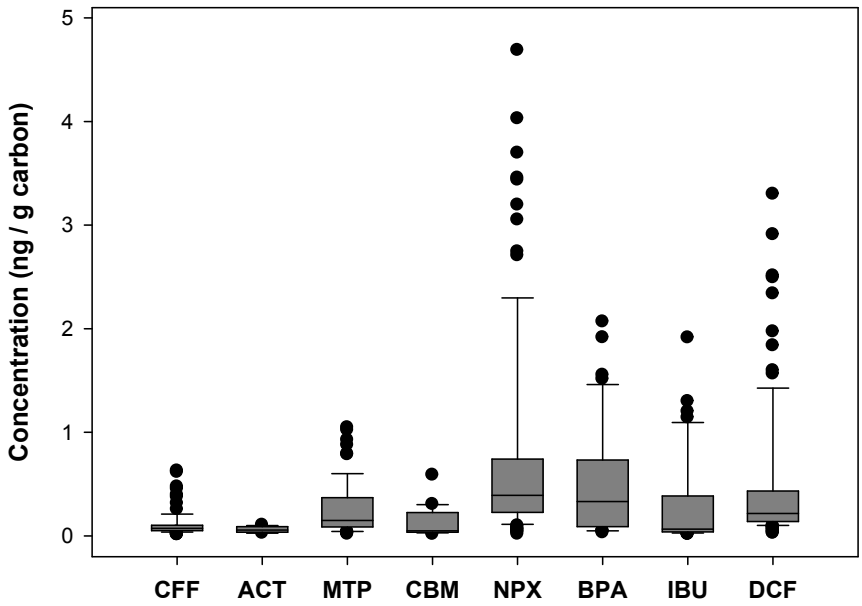

Figure 4. Distribution of micropollutants concentraion from spent activated carbon filter.

Table 11. Concentration of tap water in Korea

ng/L	CFF	ACT	SMA	SMZ	MTP	CBM	NPX	BPA	IBU	DCF	TCB
Freq.[a](%)	64.00	68.00	-[b]	-	-	8.00	100.00	100.00	16.00	100.00	4.00
Mean ± SD (ng/L)	1.42 ±1.59	1.73 ±0.38	-	-	-	0.99 ±0.67	3.28 ±2.32	13.93 ±11.76	1.12 ±0.66	4.76 ±1.81	0.67
Median (ng/L)	0.78	1.73	-	-	-	0.99	2.89	10.31	0.96	4.99	0.67
Min. (ng/L)	0.49	1.09	-	-	-	0.51	0.81	3.49	0.52	0.96	0.67
Max. (ng/L)	5.92	2.39	-	-	-	1.46	12.65	58.04	2.03	7.87	0.67

N=25
[a]Freq.=detection of frequency(%)
[b]not detectable

3.3. Comparison of micropollutants desorption amount in 4 major river basins in Korea

The regional pattern along four major river basins of desorption amount of naproxen, bisphenol-A, ibuprofen, and diclofenac with high detection frequency can be compared according to 4 big river streams. The regional pattern of micropollutants detection in the field filters was compared. The filters from the Han river basin and Nakdong river basin showed higher detection of micropollutants (Figure 5). This is due to that there are large population in mega cities such as Seoul, Busan and Daegu which are densely populated areas. In those cities, the usage of micropollutants would be much higher than other places.

Next, the desorption amount can be compared according to existence of advanced oxidation process (AOP) in water treatment plants where the filters are obtained. The advanced oxidation process in Korea is mostly ozone process followed by biological activated carbon. As shown in Figure 6, most compounds were detected lower where AOP process were applied in WTPs. Especially, caffeine, naproxen, bisphenol-A and diclofenac showed the statistical difference with significance level

($p<0.05$). The result shows those advanced oxidation process is effective in removal of micropollutants. This is in agreement with previous studies that reported biological activated carbon filtration following ozonation is effective in removal micropollutants, natural organic matter, taste and odor compounds, disinfection by-product precursors, as well as ozonation transformation products and it can also reduce non-specific toxicity in drinking water treatment (Simpson, 2008; Reungoat et al., 2010; Reungoat et al., 2012).

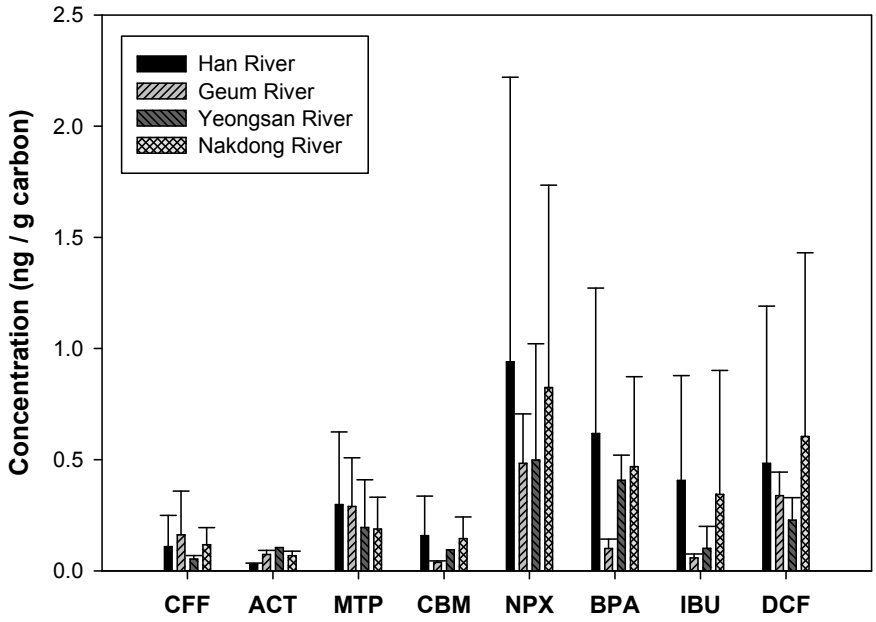

Figure 5. Comparison of desorption amount of micropollutants from filters according to 4 river basin areas.

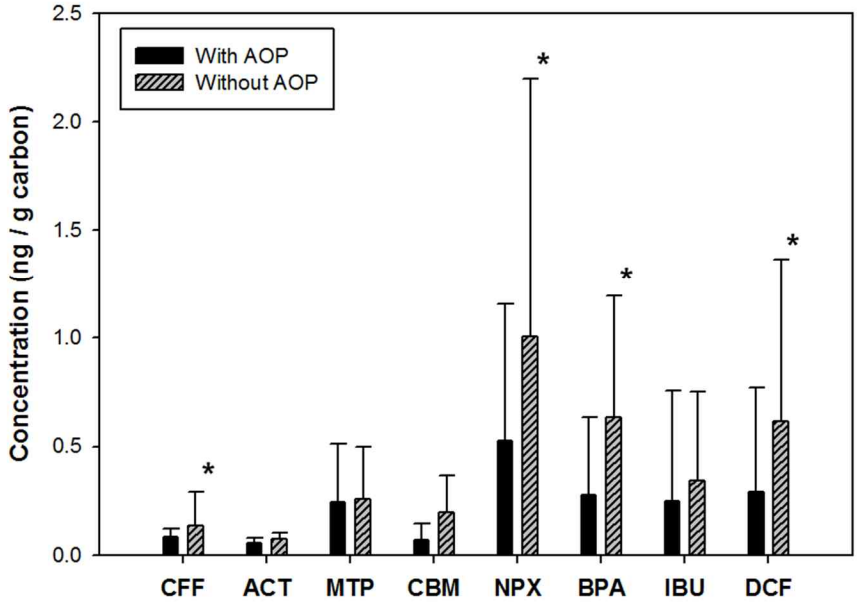

Figure 6. Comparison of desorption amount of micropollutants according to existence of advanced oxidation process in water treatment plants ($^{*}p<0.05$).

3.4. Comparison of desorption in different filters

The desorption amount of 2 different kinds of activated carbon filters was compared. Their pore size and length are different. The pore size of filter A is about 10 μm and filter B is about 1 μm, which the pore size of filter B are 10 times smaller than filter A. The length of filter A is 16 cm and filter B is 8 cm, which also means carbon amount of filter A (130 g d.w.) is about 2 times higher than filter B (60 g d.w.) (Table 6). It is known that the higher carbon amount is, the higher concentration of micropollutants adsorbed in activated carbon filter (Zimmerman et al., 2005). However, when adjusted by carbon amount, the desorption amount of small pore size filter was higher than large pore size filters (Figure 7). Therefore, it can be confirmed that the higher adsorption activity occurs with the smaller pore size filters because they have larger surface area. The enough pore volume of smaller pore size can improve the adsorption capacity of activated carbon (Mangun et al., 1999).

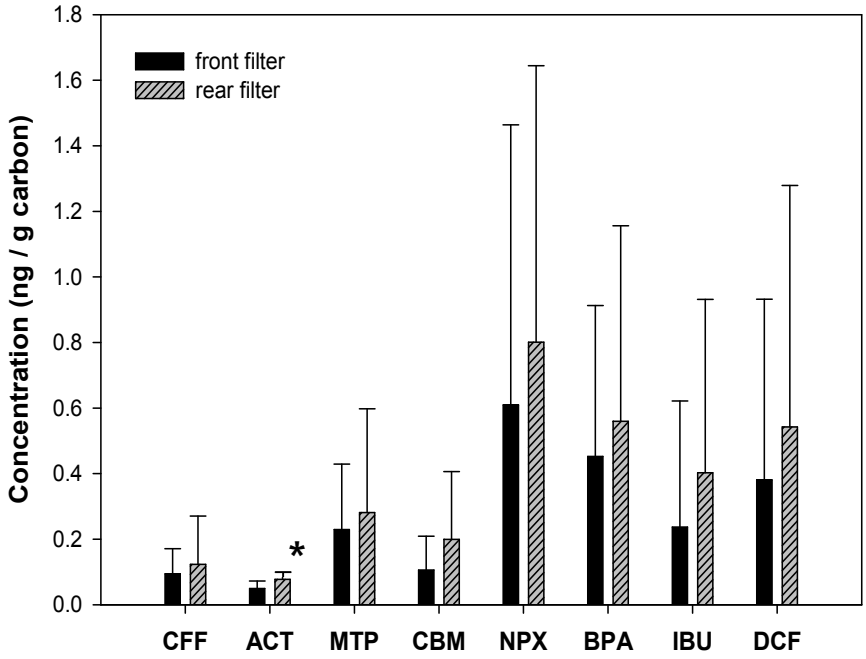

Figure 7. Comparison of desorption amount of micropollutants according to different pore size filters ($^{*}p<0.05$).

3.5. Human health risk assessment of the micropollutants

First, daily intake of PPCPs and EDCs in tap water were estimated based on tap water concentration in this study (Table 11). By applying tap water concentration of micropollutants, average drinking water ingestion rate (1.502 L/day), exposure duration (78.6 year of lifetime) and body weight (according to each age range) based on Korean Exposure factors handbook (Jang et al., 2007) to exposure assessment equation, daily exposure of ingestion intake was calculated (Table 12). Exposure levels (Estimated daily intake) for the average values of each micropollutants were higher in toddler age group, but it was still in very low level (Figure 8). All compounds have non-carcinogenic effect to human health, so the toxicity values (chronic non-cancer reference dose) of 7 compounds (caffeine, acetaminophen, sulfamethazine, metoprolol, carbamazepine, bisphenol-A, triclocarban) were refer to reference literatures. Hazard quotient was measured by dividing daily exposure value of ingestion by reference dose. Hazard quotient value was very low less than 0.0001, so it means there was almost no non-carcinogenic health effect of micropollutants via drinking tap water (Table 12). That's

because micropollutants concentration in tap water of this study was very low level so it doesn't have an adverse effect on human health.

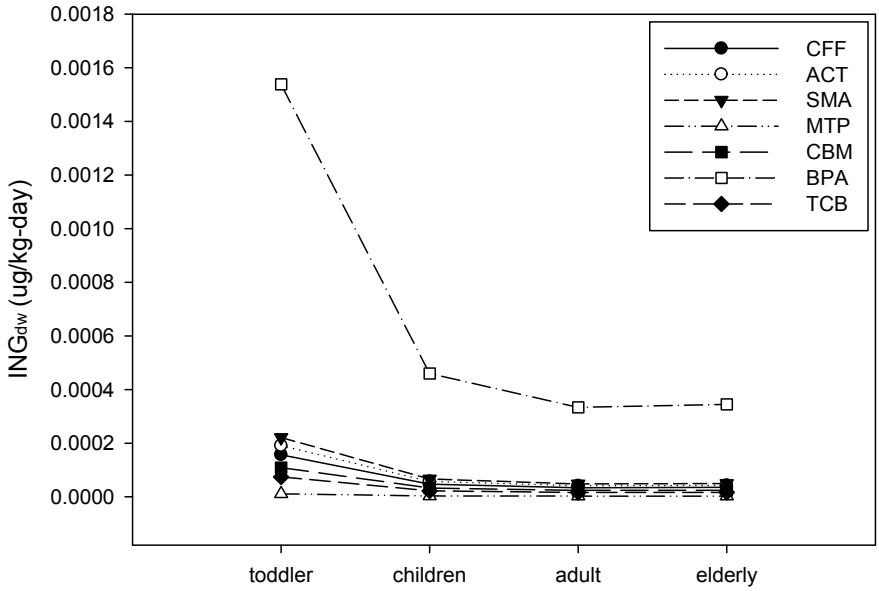

Figure 8. Estimated Daily ingestion intake for each micropollutants.

Table 12. Exposure assessment and risk assessment of micropollutants

	group	age	Body weight(kg)[a]	CFF	ACT	SMA	MTP	CBM	BPA	TCB
ING_{dw}	toddler	0-7	13.6	1.6E-04	1.9E-04	2.2E-04	1.1E-05	1.1E-04	1.5E-03	7.4E-05
(μg/kg·day)	children	8-17	45.5	4.7E-05	5.7E-05	6.6E-05	3.3E-06	3.3E-05	4.6E-04	2.2E-05
	adult	18-74	62.8	3.4E-05	4.1E-05	4.8E-05	2.4E-06	2.4E-05	3.3E-04	1.6E-05
	elderly	>=65	60.7	3.5E-05	4.3E-05	4.9E-05	2.5E-06	2.4E-05	3.4E-04	1.7E-05
RfD	(μg/kg·day)			450.00	93.00[b]	19.00[c]	14.00[d]	5.70[e]	4.00[f]	625.00[g]
HQ	toddler	0-7		3.5E-07	2.0E-06	1.2E-05	7.9E-07	1.9E-05	3.8E-04	1.2E-07
	children	8-17		1.0E-07	6.1E-07	3.5E-06	2.4E-07	5.7E-06	1.1E-04	3.5E-08
	adult	18-74		7.6E-08	4.4E-07	2.5E-06	1.7E-07	4.1E-06	8.3E-05	2.6E-08
	elderly	>=65		7.8E-08	4.6E-07	2.6E-06	1.8E-07	4.3E-06	8.6E-05	2.7E-08

[a] Korean Exposure factors handbook, Ministry of Environment. 2007
[b,C] Minnesota department of Health. 2013-2014
[d,e] Schriks et al. 2010
[f] European Food Safety Authority. 2015
[g] Snyder et al. 2013

V. Conclusion

In this study, the various conditions were compared according to desorption tool, several extraction solvents, solvent amount, and mixing time. As a result, this study found the optimized lab-scale experimental condition of PPCPs desorption from powdered activated carbon. The optimized condition is 1 g PAC, 800 mL of acetonitrile, 90 min sonication. This is cost-effective, practical, and useful method for desorption of spent activated carbon compared to other desorption method. Also, the desorption experiment of spent field water filters used in the commercial water purifiers was conducted and compared with the tap water concentration. As a result, this study could detect some micropollutants which is hardly detected if tap water is analyzed directly. Also, this study could compare amount of micropollutants in spent carbon filters according to regional factors; 4 river basin, advanced oxidation process in water treatment plants. In the filters collected from river basin where mega cities are located, the higher desorption amount of micropollutants was detected. The result also shows that advanced oxidation process (Ozone and BAC) in WTPs is more effective in

micropollutants removal than conventional treatment process. When compared according to different pore size filters, more amount of micropollutants was desorbed in smaller pore size filter, which shows smaller pore size filter can adsorb micropollutants more effectively. Also, the result of the risk assessment of drinking tap water shows micropollutants concentration in tap water doesn't have an adverse effect on human health. In further study by applying the desorption method, unknown micropollutants can be detected from spent activated carbon filters and regional properties of tap water can be compared.

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국문초록

수도수에 잔류하는 미량오염물질 규명을 위한 만기 사용한 활성탄 필터 탈착 연구

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한국에서는 수돗물을 식수로 이용하는 데 불신으로 인해 정수기 사용률이 높다. 우리나라 정수기의 대부분은 전처리, 후처리 공정으로 활성탄 필터를 이용한다. 이러한 활성탄 필터는 4~6개월 주기로 교체가 이루어지는데 이렇게 교체된 필터에는 수돗물에 잔류하는 유기물질들이 흡착되어 있을 것이기 때문에 이러한 필터를 탈착하여 분석한다면 역으로 수돗물에 어떤 물질들이 존재하는지 파악할 수 있다.

본 연구에서는 만기 사용한 필터에서 의약물질 및 생활용품, 내분비계 교란 물질을 유기용매 추출과 초음파 추출 방법을 이용해 탈착시키는 연구가 진행되었다. 본 연구에 선정된 물질들은 caffeine, acetaminophen, sulfamethazine, sulfamethoxazole, metoprolol, carbamazepine, naproxen, bisphenol-A, ibuprofen, diclofenac, triclocarban 국내 많이 유통되고 있는 11가지 물질들로 대부분의 물질들이 국내 지표수내에서 지속적으로 검출된 사례들이 보고되고 있다.

본 연구는 정수기에 사용된 활성탄 필터를 효율적으로 탈착시키는 최적화 방법을 고안하고 이를 실제 필터에 적용시켜 수도수 특성을 지역별로 비교하였다. 최적화 조건을 찾기 위해 탈착 tool, 탈착 용매, 용매 용량, 탈착 시간 등 여러 가지 조건을 비교해본 결과, 1 g PAC를 800 mL acetonitrile을 이용해 30℃에서 90분 동안 탈착시켰을 때 가장 탈착률이 높은 결과를 얻을 수 있었다. 이는 다른 열탈착, 촉매 산화법 등의 방법보다 더 경제적이고 실용적인 방법이다. 이 조건을 적용하여 전국에서 수집한 실제 만기 사용된 필터 100개를 탈착시켜 분석한 결과, caffeine, metoprolol, naproxen, diclofenac은 60% 이상의 높은 검출률을 보였고, sulfamethazine, sulfamethoxazole, triclocarban은 10% 이하의 낮은 검출률을 보였다. sulfamethazine, metoprolol, ibuprofen은 수도수 분석에서는 거의 검출되지 않았지만 필터를 탈착시킴으로써 검출할 수 있었다.

따라서 이러한 물질들은 수도수에 너무 미량으로 존재하여 검출하기 어렵지만 고농축된 필터를 탈착시킴으로써 분석할 수 있다는 것을 확인할 수 있었다.

다음으로, 지역별 차이를 보기 위해 탈착량을 지역에 따라 구분하여 4대강 유역별로 비교한 결과, 서울, 부산, 대구 등의 대도시가 위치한 한강과 낙동강 유역에서의 미량오염물질 검출량이 높은 것을 확인할 수 있었다. 다음으로 필터 수집 지역 정수처리장의 고도산화처리공정 유무에 따라 탈착량을 비교한 결과, 고도산화처리공정이 없는 지역에서 검출량이 높게 나타났다. 따라서, 정수처리공정에서 고도산화처리가 PPCPs와 EDCs와 같은 미량오염물질 제거에 더 효과적인 것으로 나타났다. 또한, pore size가 다른 필터 종류에 따라 검출량을 비교한 결과 pore size가 10배 작은 필터에서 검출량이 더 높게 나타났다. 이는 pore size가 작은 필터가 더 흡착률이 높아서 미량오염물질들이 더 많이 흡착되어 있고, 탈착량도 많은 것을 확인할 수 있었다. 마지막으로, 수도수 분석 결과를 통해 수도수 음용에 따른 위해성 평가를 실시한 결과 모두 HQ 값이 0.0001보다 낮은 값으로 인체에 위해한 수준은 아닌 것으로 나타났다.

활성탄 흡착에 관한 연구는 많이 이루어져 있지만 탈착에 관한 연구는 아직 부족한 실정이기 때문에 경제적이고 효율적인 탈착 방법을 고안해 내는 데 상당한 의미가 있다. 본 연구에서의 고농축된 필터를 탈착시키는 방법은 향후 수도수에 너무 미량으로 존재하여 분

석하기 어려운 미량오염물질들을 검출하고, 지역별 수도수 특성을 파악하는 데 유용한 방법으로 이용될 수 있을 것으로 기대된다.

주요어: 미량오염물질, 활성탄, 탈착, 최적화, 수도수

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